EXAFS study on Cu nano-clusters produced by energetic heavy ion irradiation in AlCu binary alloys

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1 Introduction
Our previous studies indicate that by the energetic ion irradiation, the surface hardness of practical aluminum alloys such as duralumin increases much faster than that induced by thermal treatments at elevated temperatures [1-3]. In the present report, we will show through the EXAFS measurement that nano-structured Cu clusters are produced by energetic ion irradiation in AlCu binary alloys.

2 Experiment
Al-2wt%Cu and Al-4wt%Cu alloys were prepared by using pure Al and Cu. The two kinds of metals (Al and Cu) were mixed in a crucible above the melting temperature. In order to obtain supersaturated alloys, the resulting ingot of AlCu alloys were thermally annealed at 833 K for 48 hours under atmosphere and then quenched into iced water. After the thermal treatment, the ingot was rolled into sheets about 1mm thick. The sheets were cut into several specimens and solution-treated at 833 K. The specimens were irradiated with 16 MeV Au ions by using a tandem accelerator at Takasaki Advanced Radiation Research Institute of National Institutes for Quantum and Radiological Science and Technology (QST-Takasaki). The temperature of the specimens were kept near room temperature during the irradiation. The irradiation fluences were from 2.5x1015/cm2 to 3x1016/cm2. For comparison, pure Al specimens were also irradiated with 16 MeV Au ions up to the fluence of 5x1015/cm2.

The Vickers hardness for irradiated and unirradiated specimens was measured with a load of 10gf. To examine atomic arrangements around Cu atoms, the extended x-ray absorption fine structure (EXAFS) was measured around the Cu-K absorption edge (8.98 keV) at the 27B beamline of the synchrotron radiation facility of High Energy Accelerator Research Organization (KEK-PF). The EXAFS spectra were obtained by using a fluorescence method with a 7-element germanium x-ray detector at room temperature. We used the computer software, WinXas for the analysis of the EXAFS spectra. All the EXAFS spectra were Fourier transformed using k3 weighting with the k range from 2-3 to 10-15 A-1.

The EXAFS simulations were performed for the following atomic arrangements; (1) a Cu atom replaced an Al atom of the Al matrix, and (2) all the nearest neighbor atoms, all the 2nd nearest neighbor atoms and all the 3rd nearest neighbor atoms of a Cu atom which replaces an Al atom are Cu atoms.

3 Results and Discussion
Fig. 1 shows the Vickers hardness as a function of ion fluence for Al-2wt%Cu, Al-4wt%Cu and pure Al irradiated with 16 MeV Au ions. The hardness of the AlCu binary alloys increases largely, while the hardness of pure Al scarcely increases even for higher ion fluence. Moreover, the increase in hardness for Al-4wt%Cu is much larger than that of Al-2wt%Cu. From such a Cu concentration dependence of the irradiation-induced hardness change, we can conclude that Cu precipitates dominate the increase in hardness of the AlCu alloys.

Fig. 1: Vickers hardness for Al-2wt.%Cu, Al-4wt%Cu and pure Al as a function of 16 MeV Au ion fluence.

Fig. 2 shows the result of the Fourier transformed (FT) EXAFS spectrum near the Cu-K absorption edge for Al-4wt.%Cu irradiated with 16 MeV Au ions to the fluence of 2.5x1015/cm2. For comparison, the spectrum for the solution-treated (unirradiated) specimen is also plotted. The intensity of all peaks in the FT spectrum decreases by the irradiation. Another effect of the irradiation on the FT spectrum is found as a rightward shift of the largest peak, which corresponds to the nearest neighbor atoms of a Cu atom in Al matrix.

A similar trend for the EXAFS FT spectrum change can be observed in the FEFF simulated spectrum for Al matrix...
including small Cu clusters. Fig. 3 shows the result of FEFF simulation for the two kinds of atomic arrangements around a Cu atom; (1) a Cu atom replaces an Al atom in FCC Al matrix, and (2) Cu atoms replace all the nearest neighbor Al atoms, all the 2nd nearest neighbor Al atoms and all the 3rd nearest neighbor Al atoms for a Cu atom in Al FCC matrix. The atomic arrangement of (1) corresponds to isolated Cu atoms in the solution treated (unirradiated) specimen, and that of (2) corresponds to small (nano-scaled) Cu clusters in the Al matrix. Therefore, the similar trend of the EXAFS spectrum change shown in Fig. 2 and Fig. 3 suggests that small Cu clusters (precipitates) are produced by the Au ion irradiation. The small Cu clusters in Al matrix play an important role in the increase in hardness of the AlCu binary alloys.

Fig. 2: EXAFS FT spectrum near Cu-K absorption edge for Al-4wt%Cu irradiated with 16 MeV Au ions. Ion fluence is $2.5 \times 10^{15}$/cm$^2$. For comparison, spectrum for solution treated (unirradiated) specimen is also shown.

4 Summary
AlCu binary alloys were irradiated with 16MeV Au ions at room temperature, and the changes in surface hardness and the local atomic structure around Cu atoms by the irradiation were investigated by using the Vickers hardness measurement and the EXAFS measurements near the Cu-K absorption edge, respectively.

The hardness of irradiated specimens increased with increasing the ion fluence. The experimental EXAFS FT spectra for the unirradiated and the ion irradiated specimens and those by the FEFF simulation suggest the irradiation-induced formation of small Cu clusters in Al matrix.

Fig. 3: Result of FEFF simulation for the two kinds of atomic arrangements around a Cu atom; (1) a Cu atom replaces a Al atom in FCC Al matrix, and (2) Cu atoms replace all the nearest neighbor Al atoms, all the 2nd nearest neighbor Al atoms and all the 3rd nearest neighbor Al atoms for a Cu atom in Al FCC matrix.

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